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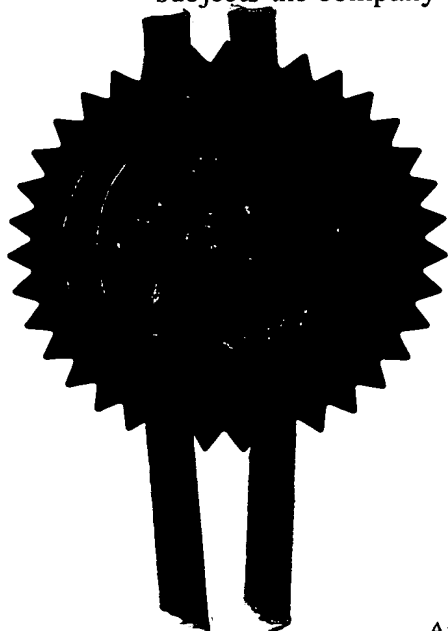
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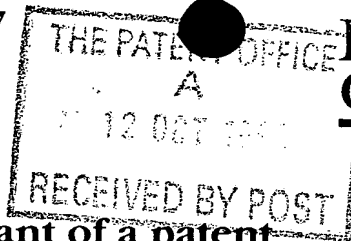
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12 OCT 1998 E396391-1 D01091  
F01/7700 0.00 - 9822083.3

# Request for grant of a patent

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Cardiff Road  
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12 OCT 1998

1. Your reference

AA 1433 GB

2. Patent application number

(The Patent Office will fill in this part)

9822083.3

3. Full name, address and postcode of the or of each applicant (underline all surnames)

JOHNSON MATTHEY PUBLIC LIMITED COMPANY

2-4 COCKSPUR STREET  
TRAFALGAR SQUARE  
LONDON SW1Y 5BQ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

536268007

4. Title of the invention

EMISSION CONTROL

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

IAN CARMICHAEL WISHART  
JOHNSON MATTHEY TECHNOLOGY CENTRE  
BLOUNTS COURT  
SONNING COMMON  
READING RG4 9NH

Patents ADP number (if you know it)

7258312001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

c) any named applicant is a corporate body.

See note (d))

**Patents Form 1/77**

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Continuation sheets of this form	0
Description	8 <i>J 84</i>
Claim(s)	3
Abstract	1
Drawing(s)	1 <i>41</i>

10. If you are also filing any of the following, state how many against each item.

**Priority documents**

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

ONE *✓*

Request for substantive examination (*Patents Form 10/77*)

Any other documents  
(*please specify*)

11. I/We request the grant of a patent on the basis of this application.

Signature

*I C Wishart*

Date *9 Oct 98*

I C WISHART

12. Name and daytime telephone number of person to contact in the United Kingdom

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EMISSION CONTROL

This invention concerns emission control systems, especially for diesel, *ie* compression-ignition, engine exhausts.

5

EP-A-0341832 describes a process and treatment system for removing soot from diesel exhaust gas containing NO by passing such gas unfiltered over an oxidation catalyst to convert NO to NO<sub>2</sub>, collecting the soot on a filter and using the resulting gas containing NO<sub>2</sub> to combust the collected soot, the amount of NO converted to NO<sub>2</sub> being sufficient to enable such combustion to proceed at a temperature less than 400°C.

10

In the process to be described the combustion step is followed by a step of removing NO<sub>x</sub> from the combustion outlet gas by means of a solid absorbent and regenerating the absorbent by intermittent contact with rich exhaust gas obtained by temporary alteration of the exhaust gas composition, for example by engine fuel inlet adjustment or injection of reductant into the exhaust gas upstream of the absorbent. It has now been realised that in a process of that type the gas from regeneration of the NO<sub>x</sub> absorber resembles the exhaust of a gasoline engine operating at equivalence or richer. Thus any remaining HC and CO in the regeneration outlet gas can be removed over a two-way catalyst system, or HC, CO and NO<sub>x</sub> over a three-way catalyst system.

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ACCORDING TO THE INVENTION

There is provided a process for treating combustion exhaust gas containing CO, HC, NO, O<sub>2</sub>, soot and non-reactive gases, by the steps:

25

- (i) catalysing oxidation of said NO to NO<sub>2</sub>;
- (ii) collecting soot on a filter from the product of (i);
- (iii) combusting said soot by reaction with said NO<sub>2</sub>, and possibly also any O<sub>2</sub> left over after the reactions in (i);
- (iv) removing NO<sub>x</sub> from the product of (iii) by the action of a regenerable NO<sub>x</sub> absorbent; and
- (v) regenerating said absorbent by intermittently decreasing the net oxidant level;

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(vi) at least during said regeneration, passing the gas leaving the absorbent over the catalyst system effective to promote reactions of HC and CO with O<sub>2</sub> to H<sub>2</sub>O and CO<sub>2</sub>. Preferably, the catalyst system in step (vi) is effective also to react NO<sub>x</sub> to N<sub>2</sub>.

5 The invention therefore provides a treatment system for such exhaust gas comprising catalysts and absorbent corresponding to said process steps, in particular, in combination and in order:

- (a) catalyst effective to promote oxidation of at least NO to NO<sub>2</sub>;  
a filter effective to collect said soot and hold it for combustion reaction with the  
10 NO<sub>2</sub> in the gas;  
a NO<sub>x</sub> absorber charged with solid absorbent;  
means for introducing reductant intermittently upstream of said absorber; and,  
downstream of said absorber;  
a catalyst system effective to promote reactions of HC and CO with O<sub>2</sub> to H<sub>2</sub>O and  
15 CO<sub>2</sub> and preferably with NO<sub>x</sub> to N<sub>2</sub>.

In addition, the system may include routine features, for example, means to adjust the temperature of the gas to the level required in the next downstream chemical step.

20 The system may be structured within a single housing ("can"), or in separated housings according to engine design and under-floor or other space considerations. Thus, for example, for V-engine configurations, some, or all, of the elements of the system may be disposed in parallel.

25 The catalysts and absorbent are suitably supported on a ceramic or metal honeycomb, the ceramic comprising one or more of alumina, silica, titania, cordierite, ceria, zirconia, silicon carbide or other, generally oxidic, material. The honeycomb carries a washcoat and, in one or more layers thereon, is the active catalytic and/or absorptive material, to be described in more detail below. The honeycomb has typically at least 50 cells  
30 per square inch, possibly more, eg up to 800, or 1200, if composed structurally of metal. Generally, the range 200-800 is preferred for the catalysts and absorbent.

In the oxidation catalyst the active material comprises generally a platinum group metal ("PGM"), especially platinum and/or palladium, optionally with other PGMs, eg rhodium, and other catalytic or promoting components. The exact compositions and structure of the oxidation catalyst is not critical to operation of the invention, and hence may be varied according to the requirements of the situation. A low temperature light-off formulation is generally preferred. Conventional manufacturing techniques may be used. The catalyst should of course be sized and composed to achieve the necessary conversions, and should minimise trapping of soot within its honeycomb.

The filter may be any capable of trapping the soot without causing excessive back-pressure. In general, ceramic, sintered metal or woven or non-woven wire filters are usable, and wall-flow honeycomb structures may be particularly suitable. The structural material of the filter is preferably porous ceramic oxide, silicon carbide or sintered metal. A coating such as alumina, and also a catalyst such as La/Ca/V<sub>2</sub>O<sub>5</sub> may be present. The soot is generally carbon and/or heavy hydrocarbons, and is converted to carbon oxides and H<sub>2</sub>O. Certain embodiments of this principle are in commercial use in Johnson Matthey's Continuously Regenerating Trap technology, and are described in US 4902487, the teaching of which is incorporated herein by reference.

The NO<sub>x</sub> absorbent may comprise also a catalyst, as described further below. It may be provided in one unit or a succession of separate units. It may be in the form of active layers on a conventional honeycomb substrate, or may be in the form of serial deposits on a single honeycomb or possibly multiple honeycombs.

The absorbent may be selected from:

- (a) compounds of alkali metals, alkaline earth metals, rare earth metals and transition metals, capable of forming nitrates and/or nitrites of adequate stability in absorbing conditions and of evolving nitrogen oxides and/or nitrogen in regenerating conditions;
- (b) adsorptive materials such as zeolites, carbons and high-area oxides.

Compounds (a) may be present (before NO<sub>x</sub> absorption) as composite oxides, eg of alkaline earth metal and copper such as Ba-Cu-O or MnO<sub>2</sub>-BaCuO<sub>2</sub>, possibly with added

Ce oxide, or Y-Ba-Cu-O and Y-Sr-Co-O. (The oxides are referred to for simplicity, but in practice hydroxides, carbonates and nitrates are present, depending on the temperature and gas composition). Whichever compounds are used, there may be present also one or more catalytic agents, such as precious metals, effective to promote such reactions as the interchanges of the nitrogen oxides and the action of reductants.

The catalyst system for the step (vi) can be any that is active at the prevailing temperature and not adversely affected by exposure to lean gas between regeneration periods. Typically it comprises one or more PGMs, especially Pt, Rh, Pd and combinations thereof, on a high-surface washcoat on a honeycomb structure as described above. Many others have been described in the literature and are available to skilled persons.

For regeneration of the  $\text{NO}_x$  absorber:

1. Hydrocarbon reductant may be introduced, for example gasoline or diesel fuel, which is especially convenient, or another such as light oil, kerosene or a  $\text{C}_3$  to  $\text{C}_8$  paraffin;
2. A preferred technique comprises injecting hydrogen (suitably generated *in situ* on board the vehicle) or a readily dehydrogenatable reductant such as a lower alcohol, especially methanol or ethanol.
3. Another preferred technique comprises injecting a  $\text{NO}_x$ -specific reactant, especially ammonia or hydrazine. This can be injected as such or as a solution in *eg* water or as a compound producing the reactant in exhaust treatment conditions, for example urea or aqueous urea solution.

Decrease of net oxidant level can be by for example:

1. Engine management, suitably by inlet air flow throttling or by an additional fuel injection during the time period in which regeneration gas is required. The additional fuel injection, whether to each or possibly as few as one cylinder, should be in the exhaust phase of the diesel cycle, to avoid torque shock;
2. Injection of reductant upstream of the oxidation catalyst. The injection point may be at the engine outlet or may be at the inlet of the catalyst system;
3. Injection of reductant between the oxidation catalyst and the filter;



Injection of reductant between the filter and the absorbent. This provides least interference with soot combustion.

The gas composition resulting from oxidant level decrease corresponds suitably to an air/fuel weight ratio in the range 10 to equivalence.

Control of the means to regenerate the  $\text{NO}_x$  absorber includes for example the following:

1. Injection responsive to ultimate detection of  $\text{NO}_x$  leakage from the absorber;
2. Injection responsive to prediction based on input of data on deliberate or load-responsive engine management variation;
3. Allowance for gas composition variations, for example non-steady conditions such as incomplete warm-up or weather.

Usually the regeneration phase can be a small fraction of engine running time, *eg*, 0.1% to 5%, depending of course on operating conditions.

The invention provides also an engine in combination with a system as herein defined and a process of operating such an engine.

The combination may include established expedients such as EGR, or recycle of released  $\text{NO}_x$  to one or more points upstream of the soot filter.

The combination may include sensors for at least one of:

fuel composition;  
air/fuel ratio;  
exhaust gas compositions and temperatures at critical stages;  
pressure drop, especially over the filter.

It may include also indicator means informing the engine operator, computer means effective to evaluate the data from the sensor(s), and control linkages effective to adjust the

engine to desired operating conditions taking account of *eg* start-up, varying load and fluctuations.

Preferably the engine is a diesel engine, although other engines, including direct injection gasoline engines, may also benefit from the invention. The engine may be the motive power for a vehicle, or may be a stationary power source or auxiliary power source. It may be for a "heavy duty" vehicle, *ie* at least 3500kg, or a "light duty" vehicle, including in particular a passenger car or light van and likely to be operated according to the "urban cycle".

Desirably, the engine is fuelled with low-sulphur fuel, *ie* having less than 50ppm of sulphur, by weight as elemental S.

For operation with higher sulphur fuels, a SO<sub>x</sub> absorbent may be used at some stage upstream of the NO<sub>x</sub> absorber.

One preferred form of the invention will now be described by way of example, with reference to the accompanying schematic drawing.

The system consists of single "can" 10, which is connected at 12 to the exhaust from a diesel engine (not shown) fuelled with diesel oil of under 50ppm sulphur content. At the inlet end of can 10 is catalyst 14, which is a low temperature light-off oxidation catalyst supported on a 400 cells/in<sup>2</sup> ceramic honeycomb monolith. Catalyst 14 is designed to be capable of meeting emission regulations in relation to CO and HC for the engine and vehicle and also converts at least 70% of the NO to NO<sub>2</sub>.

The gas leaving catalyst 14 passes into soot filter 16, which is of the ceramic wall flow type and collects particles over 50nm?. The NO<sub>2</sub> and surplus oxygen in the gas oxidise the soot at temperatures around 250° C with no accumulation or tendency to blocking.

The gas leaving filter 16 is passed over sparging spray injector 18, from which it may receive liquid reductant from supply tank 20 *via* line 22. Injector 18 is fed by pump 24 under the control of engine management system 26. Pump 24 suitably acts in a pulse mode.

The gas from 18, possibly reductant-carrying, then enters NOx absorber 28. During normal lean operation of the engine and without reductant injection at 18, the NOx absorber substantially removes all NOx flowing. When, however, gas enriched with reductant reaches it, the NOx is released, and may be converted to N<sub>2</sub> to some extent. The gas, now containing reductant, NOx and O<sub>2</sub>, passes into three-way catalyst 30, where these reactants are brought substantially to chemical equilibrium as non-polluting gases.

The process and system of the invention is expected to be capable of meeting European Stage IV emission legislation, with all regulated emissions comfortably within the standards set.

### **EXAMPLE 1**

#### **NOX-TRAP REGENERATION WITH DIESEL FUEL**

A NOx-trap comprising a 400cpsi monolith having wall thickness of 6/1000 of an inch, measuring 5.66 x 6 inches, carrying a coating containing barium (13.2%), platinum (1.7%), rhodium (0.17%), with minor proportions of alumina, ceria and zirconia with a total loading of 3.5g/in<sup>3</sup> was subjected to a CRT-treated gas stream from a 1.9 litres naturally-aspirated direct injection diesel engine (Swedish MK-1 fuel) containing NOx (260ppm) at a catalyst inlet temperature of 310°C for 30 seconds during which time it began to become saturated with stored NOx. Upon introduction of MK-1 diesel fuel into the exhaust gas stream in front of the NOx-trap at a rate of 1g/s for 3 seconds, the NOx-trap regenerated, such that it was able to store NOx once more. The original operating conditions were restored whereby the same amount of NOx was stored, and this process was repeated many times without deterioration of the NOx capacity of the trap.

## **EXAMPLE 2**

### **NOX-TRAP REGENERATION WITH EGR + FUEL INJECTION**

5           A NOx-trap as Example 1 was subjected to CRT-treated gas stream containing NOx (145ppm) at a catalyst inlet temperature of 220°C for 30 seconds during which time it stored NOx. The engine was as in Example 1, with EGR to reduce the oxygen concentration in the gas stream. MK-1 Diesel fuel was introduced into the gas stream in front of the NOx-trap at a rate of 1g/s for 1.5 seconds, to regenerate the NOx-trap; it was able to store NOx once  
10           more. The original operating conditions were restored whereby the same amount of NOx was stored, and this process was repeated many times without deterioration of the NOx capacity of the trap.

          Analogous successful runs were performed at other temperatures between 180°C  
15           and 330°C, with fuel injection for different times.

## **EXAMPLE 3**

### **NOX-TRAP REGENERATION WITH AMMONIA**

20           A NOx-trap as Example 1, but also including palladium (1.7%) was subjected to a synthetic CRT outlet gas stream containing NOx (100ppm) O<sub>2</sub> (9.55), CO<sub>2</sub> (8.2%) and H<sub>2</sub>O (9%) at catalyst inlet temperatures from 200 to 300°C for 60 seconds during which time it began to saturate with stored NOx. Upon introduction of ammonia (500ppm) and  
25           cutting off O<sub>2</sub> to give a reductant rich gas stream for 60 seconds, the NOx-trap regenerated, such that it was able to store NOx once more. The original operating conditions were restored as Example 1.

          In each Example the NOx-trap outlet gas became net-rich during the regeneration  
30           period and was at a temperature at which a three-way Pt/Rh catalyst would decompose NOx, HC and CO present in it.

**CLAIMS**

1. A process for treating combustion exhaust gas containing CO, HC, NO, O<sub>2</sub>, soot and non-reactive gases, by the steps:

- 5 (i) catalysing oxidation of said NO to NO<sub>2</sub>;  
(ii) collecting soot on a filter from the product of (i);  
(iii) combusting said soot by reaction with said NO<sub>2</sub> and possibly also any O<sub>2</sub> left over after the reactions in (i);
- 
- (iv) removing NO<sub>x</sub> from the product of iii by the action of a regenerable NO<sub>x</sub> absorbent; and  
10 (v) regenerating said absorbent by intermittently decreasing the net oxidant level upstream of said absorbent;  
(vi) at least during said regeneration, passing the gas leaving the absorbent over a catalyst system effective to promote reactions of HC and CO with O<sub>2</sub> to H<sub>2</sub>O and CO<sub>2</sub> and  
15 preferably also with NO<sub>x</sub> to N<sub>2</sub>.

2. Process according to claim 1 in which the catalysts and absorbent are supported on a ceramic or metal honeycomb, the ceramic comprising one or more of alumina, silica, titania, cordierite, ceria, zirconia, silicon carbide or other, generally oxidic, material and  
20 coated on the washcoat, in one or more layers, the active catalytic and/or absorptive material.

3. Process according to claim 2 in which the cell density of the honeycomb is 200-800 per square inch.

25 4. Process according to any one of the preceding claims in which the catalyst in step (i) comprises one or more platinum group metals.

5. Process according to any one of the preceding claims in which the filter comprises porous ceramic oxide, silicon carbide or sintered metal.

30 6. Process according to any one of the preceding claims in which the NO<sub>x</sub> absorber comprises:

- (a) compounds of alkali metals, alkaline earth metals, rare earth metals and transition metals, capable of forming nitrates and/or nitrites of adequate stability in absorption conditions and of evolving nitrogen oxides and/or nitrogen in regeneration conditions;
- (b) adsorptive materials such as zeolites, carbons and high-area oxides.

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7. Process according to any one of the preceding claims in which the catalyst in step (vi) comprises one or more PGMs, especially Pt, Pd, Rh and combinations thereof, on a high-surface washcoat on a honeycomb structure.

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8. Process according to any one of the preceding claims in which the reductant is introduced after step (iii).

9. Process according to any one of the preceding claims in which the reductant is a hydrocarbon, for example gasoline, diesel fuel, light oil, kerosene or a C<sub>3</sub> to C<sub>8</sub> paraffin.

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10. Process according to any one of claims 1 to 8 in which the reductant is ammonia or hydrazine and is injected as such and/or as a compound decomposable thereto *in situ*.

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11. Process according to any one of the preceding claims in which the exhaust gas is the product of combustion of a fuel containing less than 50ppm w/w of sulphur.

12. System for treatment of combustion exhaust gas having integers corresponding to the process according to any one of the preceding claims.

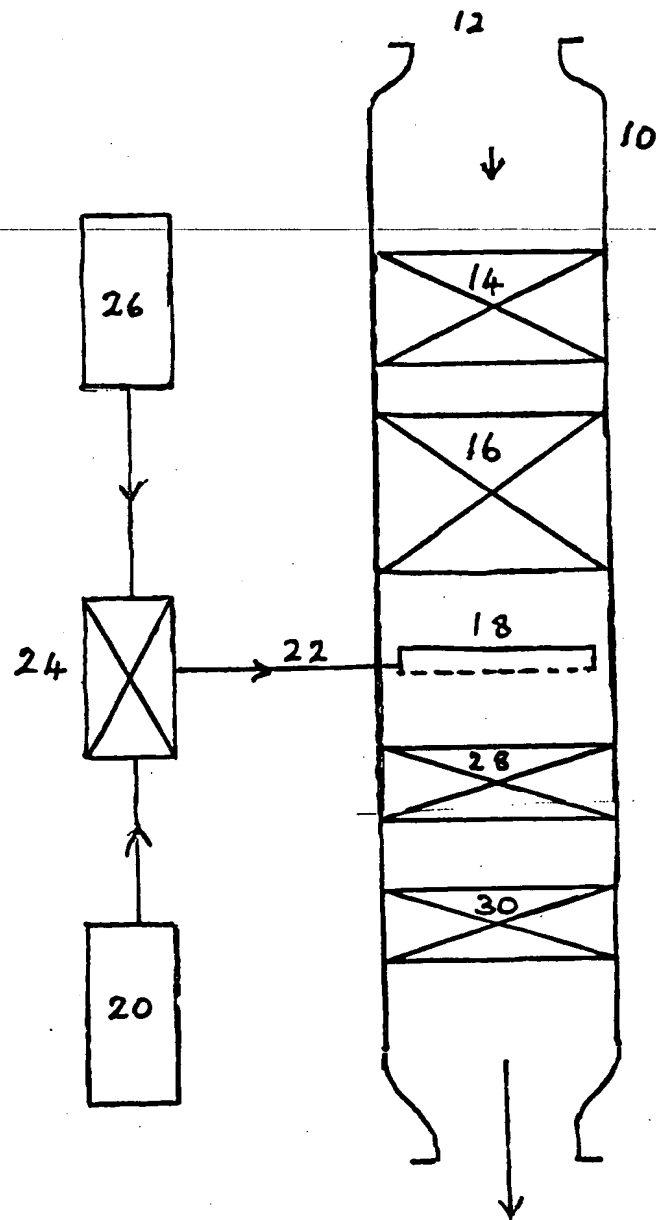
13. System according to claim 12 comprising, in combination and in order:  
a catalyst effective to promote oxidation of at least NO to NO<sub>2</sub>;  
a filter effective to collect said soot and hold it for combustion reaction with the  
NO<sub>2</sub> in the gas;  
5 a NOx absorber charged with solid absorbent;  
means for introducing reductant intermittently upstream of said absorber; and,  
downstream of said absorber,  
a catalyst system effective to promote reactions of HC and CO with O<sub>2</sub> to H<sub>2</sub>O and  
CO<sub>2</sub> and preferably also with NOx to N<sub>2</sub>.
- 10 14. A diesel engine having a system according to claim 12 or claim 13 connected to its  
exhaust.
- 15 15. An engine according to claim 14 which is of the turbo-charged direct injection type.
16. A process, system or engine according (as appropriate) to any one of the preceding  
claims, including sensors, indicators, computers and actuators, effective to maintain  
operation within desired conditions.
- 20 17. A process, system or engine substantially as described and as illustrated by the  
foregoing specific description.
18. A process, system or engine according (as appropriate) to any one of the preceding  
claims, operated in compliance with the European IV standard.

## **EMISSION CONTROL**

### **Abstract of the Invention**

5           The exhaust from a diesel or gasoline direct injection engine is passed through an oxidation catalyst (14) to convert NO to NO<sub>2</sub>, soot is collected on a filter (16) the soot is combusted by reaction with NO<sub>2</sub>, and residual NOx in the gases is absorbed by passing through a regenerable NOx absorbent (28). The absorbent is regenerated by intermittently decreasing the net oxidant level upstream of the absorbent, *eg* by injecting reductant through  
10 injector (18), and the gas leaving the absorbent is, at least during regeneration, passed over a catalyst system (30) to remove HC, CO and, preferably, NOx.





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Johnson Matthey Technology Centre

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